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The non-planarity of the enol tautomer of phosphorus-substituted pentane-2,4-dione. Influence on hydrogen bonding strength, enol content and enthalpic stabilization

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Abstract

The X-ray crystal structure of 2-(2′,4′-dioxo-3′-pentyl)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (II) reveals significant half-chair distortion of the axially oriented cis-enol ring and the tilt of the methyl groups in the enol ring away from the phosphorinane internal oxygen atoms due to their repulsive interactions. The molecule also undergoes in-plane deformations. $R(O\cdots O) = 2.410$ Å in the enol moiety indicates very strong hydrogen bonding. The enol form, δ_{OH} and stereochemical assignments were obtained from ^1H and ^{31}P NMR and IR measurements in comparison with the planar 4,6-dimethyl isomer (I) containing an equatorially oriented enol ring. The value of ΔH° for the axial–equatorial conformational equilibrium in CH_2Cl_2 was found to be -0.440 ± 0.100 kcal mol^{-1} in favour of the non-planar enol. Thermodynamic parameters for the keto–enol equilibrium in the isomeric compounds (I) and (II) were obtained in CH_3CN providing evidence for a smaller enthalpy of enolization of the non-planar enol.

1. Introduction

The planarity of β-dicarbonyl rings provides the optimum geometry for significant hydrogen-bond strengthening by delocalization of the π-conjugated system [1–5]. This conception is based upon a growing number of structure determinations of non-overcrowded enols [1–4, 6–8]. The distortion in aromatic structures is usually engendered by steric overcrowding of substituents, or by restrictive trans-ring bridges [9]. Unfortunately, the introduction of bulky alkyl substituents on the central carbon of the β-dicarbonyls depresses the enol content almost to zero [10, 11]. Even in this case the enol ring was considered as planar [1, 2, 12, 13], since downfield δ_{OH} shifts were observed in the ^1H NMR spectra.

We have recently reported [14] that phosphorus-containing bulky substituents are the most suitable for producing steric pressure on β-substituents without decreasing enolization because of their electron-withdrawing properties. The introduction

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